**Contribution of Zinc Oxide and Halloysite Nanotubes in Epoxy Coating for Corrosion Protection**

by

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22627

Dissertation submitted in partial fulfilment of

the requirements for the

Bachelor of Mechanical Engineering

With Honours

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Universiti Teknologi PETRONAS

32610 Seri Iskandar

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(MECHANICAL)

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January 2020

## CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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MUHAMMAD MUAZ BIN YAZIB

## ABSTRACT

Corrosion is a major problem which contribute to failure and give impact to the integrity of equipment and pipeline especially in oil and gas industries. Therefore, several methods such as protective coating need to be applied to prevent the corrosion. However, protective coating still have possibilities of being harmed to cracks during its service life. Several methods have been introduced to improve the coating such as addition of nanocomposite materials or nanofillers. Zinc Oxide (ZnO) is an example of nanofillers that widely used in many applications. However, it is not effective to add nanofillers directly into the protective coating. This problem can be overcome by the uses of carrier to encapsulate the nanofillers. Halloysite nanotubes (HNT) have been reported as a prominent carrier because of their good properties. The aim of this project is to investigate and evaluate the anticorrosive properties of modified epoxy coating that contains nanofillers of ZnO loaded with HNT. Thus, a few test studies such as Electron Impedance Spectroscopy (EIS) and Scanning Electron Microscopy (SEM) were conducted to achieve the goals of this project. The morphology of the coatings were investigated by SEM before and after immersion in NaCl. Moreover, EIS was conducted to evaluate performance of corrosion protection for modified epoxy coating at different concentration of ZnO-loaded HNT which are 1 wt%, 5 wt% and 10 wt%. The specimen with 100wt% of epoxy resin mixed with hardener also was formulated and evaluated by EIS as comparison to modified coating. High coating resistance was measured for all type of coating in the early staged of immersion, indicating excellent corrosion protection. As time elapsed, the coating resistance continuously decreased. After 15 days of immersion, measurements from EIS showed that neat epoxy was the worst and epoxy containing 10 wt% ZnO-loaded HNT was the best coating respectively in this project. In addition, CEP10 also showed the smoother surface in SEM compare to another coatings after the immersion.

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## LIST OF ABBREVIATION

| | |
|---|---|
| HNT | Halloysite Nanotubes |
| ZnO | Zinc Oxide |
| EIS | Electrochemical Impedance Spectroscopy |
| SEM | Scanning Electron Microscope |
| EP | Neat Epoxy Coating |
| CEP1 | Epoxy coating contains ZnO-loaded HNT at 1 wt % |
| CEP5 | Epoxy coating contains ZnO-loaded HNT at 5 wt % |
| CEP10 | Epoxy coating contains ZnO-loaded HNT at 10 wt % |

# CHAPTER 1

# INTRODUCTION

## 1.1 **Background**

Nowadays, the world is highly concerned about the deterioration of metal structures. Statistics by NACE International showed that the cost for negative impact of corrosion to the world would be 2500 billion which equivalent to 3.4 percent of global Gross Domestic Product (GDP) in 2013 [1]. Generally, corrosion is the degradation of materials due to it reaction with the environments. Corrosion inhibitors and protection coating are example of the method that widely used in industries to prevent the corrosion. Moreover, protective coating is recognized method in many studies as an effective method for corrosion protection because it can give protection to the metal that located at the above or below ground [2].

Even though coating provide good protections, it also may face some failures during their service life. Coating may damage because of external impact which might causes crack. Thus, corrosion will happen as the surface of the protecting areas which are exposed to the corrosive environments. In addition, it is very hard to identify and repair the tiny cracks [3].

Coatings can be modified by addition of nanofillers to improve their ability to prevent the corrosion of the materials. Good properties of nanofillers may have more than one function in coatings. Those nanofillers strengthen the barrier and resistance of the coating from corrosion [4]. Besides that, they also reduce rate of material deterioration, by lowering diffusion rate or minimizing effected corrosion surface [5]. Thus, this project aims in evaluating performance of epoxy coating with Halloysite Nanotubes and nanofillers, Zinc Oxide for corrosion protection.

## 1.2 Problem Statement

Epoxy coating will have reduction in barrier protection during its service life due to cracks and other mechanical failure. Thus, water, oxygen, and ionic molecules will easily diffuse into the coating barrier and causes the protected metal to corrode. The diffusion of corrosive species into the coating lower the corrosion protection performance of the coating.

The application of nanofillers such as Zinc Oxide(ZnO) may improve the performance of the coating in prevent the corrosion but direct addition of nanofillers into the coating is ineffective because they are easily washed away, creating micropores in the coating [6]. Hence, nanocontainer such as Halloysite Nanotubes (HNT) has been uses as a carrier as the alternatives to enhance the protective coating. Recently, there is still lack of studies about the application of HNT and ZnO effects the coating performance in term of corrosion protection.

## 1.3 Objectives

The objectives of this study are as follows:

- To evaluate performance of epoxy coating Zinc Oxide-loaded HNT for corrosion protection through Electrochemical Impedance Spectroscopy (EIS).
- To investigate anticorrosion protection properties of epoxy coating contains Zinc Oxide-loaded HNT.

## 1.4 Scope of Study

To accomplish the objectives of this project, the works must be carried out in the following scopes:

- Carbon steel A106 was used as metal specimen.
- Vacuum method was conducted to load ZnO into HNT.
- Epikote-828 as coating matrix and LS-D308 as hardener were used.
- The modified coatings were prepared by adding the ZnO-loaded HNT with different concentrations of 1wt%, 5wt%, and 10wt%.
- The coatings were evaluated through EIS method in 3.0wt% of NaCl solution. Furthermore, the coatings were characterized by SEM.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Corrosion Impact in Industries

NACE-International stated that the cost for negative impact of corrosion is estimated to be at 2500 billion USD that is equal to 3.4 percent for global GDP of 2013 [1]. Moreover, corrosion is a big problem in many sectors such as oil and gas sector. There are always been many issues of corrosion in refineries plant. In addition, it is very significant to manage the corrosion on global basis in order to reduce the bad impact up to 35% which equal for US$ 875 billion annually. Besides that, the service life of the equipment also could be extended by properly control the corrosion.

Corrosion may be described as the deterioration of a material due to their reaction with the environment [7]. Furthermore, corrosion need to be managed crucially especially when the products are corrosive. This can cost a lot of money in early stage for corrosion protection material design, but it will give a positive result on safety and environments. More than 25% of issues occurred in plant refineries and offshore are related to corrosion which usually caused by corrosive products such as sweet crude (CO2) and sour crude (H2S) [8].

## 2.2 Corrosion Protection Methods

Corrosion prevention methods are significant to reduce corrosion where they provide resistance to metal from undergo corrosion. Application of coating and corrosion inhibitors are the examples method to avoid the corrosion. There are a lot of methods have been developed to control the corrosion as described in Table 2.1.

In cathodic protection, metal is being protected by connecting it to another metal which is more anodic based on the galvanic series. Examples of cathodic protection are impressed current and galvanic sacrificial anode. For impressed current, anode and cathode are linked to external direct current power source. Additionally, material which can discharge current in huge amounts and hence still have a long-life expectancy is being used for the anode in ideal impressed current systems. Besides

that, galvanic sacrificial anode is the method where an active metal such as magnesium is electrically connected with metal to be protected known as cathode in the corrosive environment. Cathode is the metals that are less active compare to anode in galvanic series.

Moreover, corrosion also can be controlled by barrier protection such as paint and coatings. Protective coating is being applied on the metal surface in barrier protection and act as a protective layer between the environment and protected metal.

Table 2. 1: Corrosion Prevention Methods [9]

| Mitigation strategy | Options |
|---|---|
| Material Selection | Application of corrosion resistant alloys and non-metallic materials such as reinforced composite and polyethylene pipelines. |
| Chemical treatment | Use of vacuum deaeration, corrosion inhibitors, oxygen scavengers, and also gas blanketing. |
| Protective Coating | Protection of metal with organic coatings, paints and metallic coatings. |
| Cathodic protection | Application of sacrificial anodes and impressed current. |
| Process control | Recognizing key parameters such as temperature, pressure, flow rate, water chemistry, pH, chlorides, dissolved metals, bacteria, suspended solids, chlorine, oxygen, and chemical residuals |

### 2.2.1 Protective Coating

In order to extend the life of the materials and equipment, protective coating functions as a barrier to prevent material and the environment from directly contact. Examples of protective coatings are coating and paint [10].

According to Ahmad, the flow of electric current is reduced by the application of high resistivity coatings such as epoxies resin and vinyls [11]. Furthermore, the higher the coating thickness, the greater the electrical resistance for the coating. Therefore, there would be a much greater resistance for the current to flow.

Thus, by raising the electrical resistance of materials through coating provides an effective strategy of corrosion prevention. Coatings may be classified in a few categories is presented in Figure 2.1.

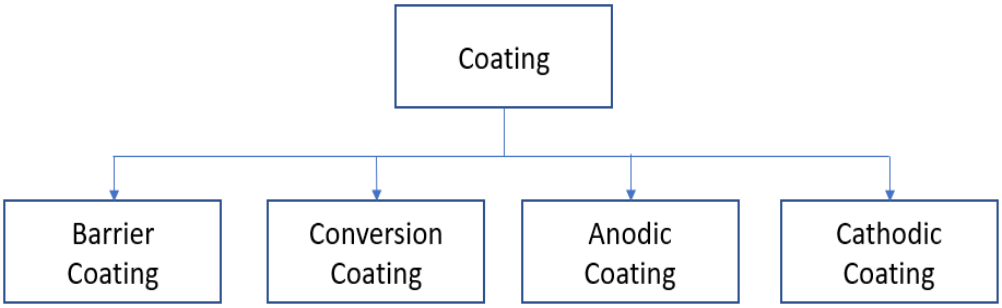



Figure 2. 1: Coatings classification [11]

### 2.2.2 Epoxy Coating

Generally, epoxy resins are most commonly used in the application of coatings cause of their good mechanical and chemical properties to most metals and alloys. Epoxy resins have been used widely in various application, as shown in Figure 2.2.

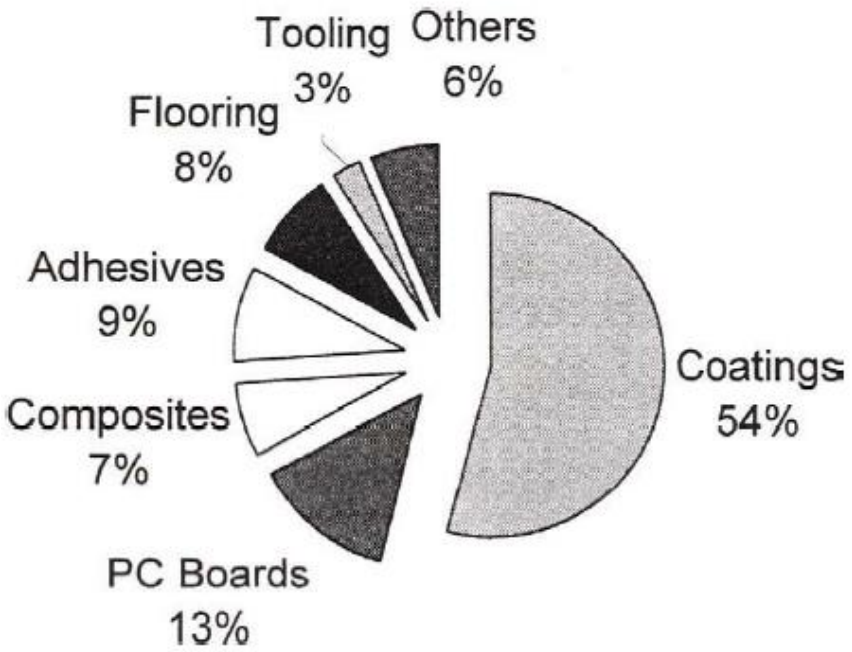



Figure 2. 2: Comparison for application of epoxy resin in industries [12]

Epoxy resins are the materials which being known by having one or more oxirane groups. Oxirane groups are shown in Figure 2.3. Moreover, epoxy resins can be divided into three major types which are cycloaliphatic epoxy resins, epoxidized oils and glycidated resins [13].

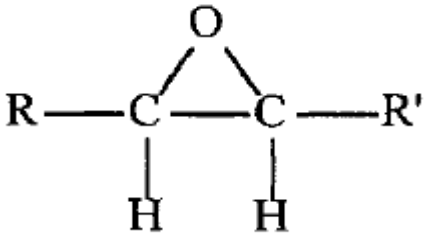



Figure 2. 3: Oxirane groups [13]

In addition, epoxy resins are a part of monomeric or oligomeric component. They also have a strong chemical and solvent resistance with spectacular adhesion [13]. Diglycidyl ether of bisphenol A, DGEBA as presented in Figure 2.4 is the most generally used resin in industries.

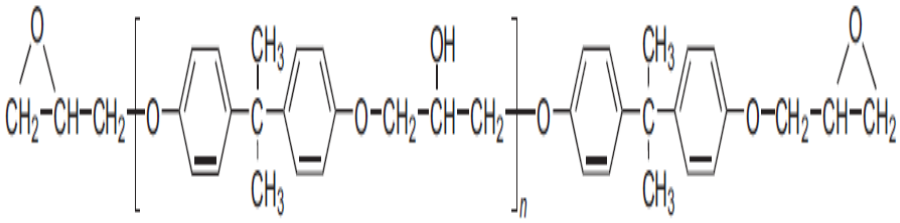



Figure 2. 4: Diglycidyl ether of bisphenol A (DGEBA) [12]

Moreover, epoxies are high performance resins and widely acceptance even though they are more costly compare to other resinous materials. This is because of their good performance in corrosion resistance and have been established as premium coatings. By interacting with curing agents, epoxy coatings receive their excellent properties. Epoxy resin reaction of curing agents with epoxy and hydroxyl properties creates extremely chemical- and solvent-resistant films [13]. The function of epoxy resins in coating is summarized in Figure 2.5.

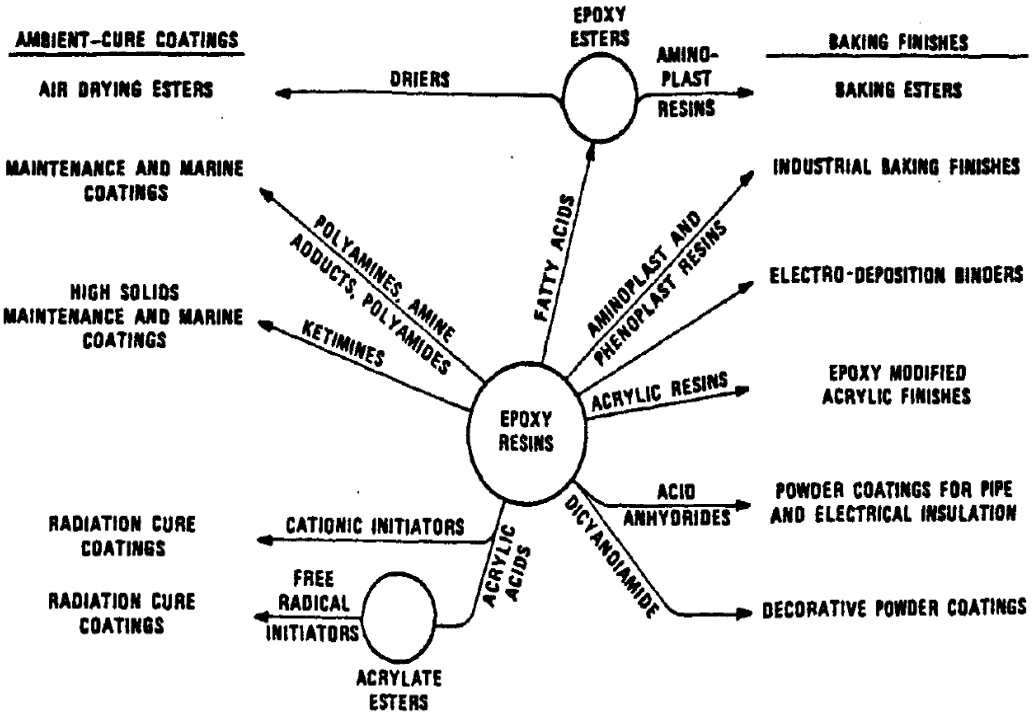



Figure 2. 5: Functions of epoxy resins in coating [13]

Epoxy have many advantages as a coating, which elaborated below: (1) Adhesion properties. Presence of hydroxyl group is the reason for epoxy to have high adhesion to metal, glass and ceramics materials. (2) Cohesion. The proper curing process will increase the cohesion strength of the epoxy. (3) Resistance to moisture and solvents. The moisture resistance of epoxy resins are higher than other resin. (4) Low creep. Epoxy will steady in their shape under prolonged stress and showing little creeep. (5) Temperature resistance. Cured solid of epoxy can be stable and be used until 2000C. (6) Low shrinkage. Epoxy resin has low shrinkage compare to other resin due to the curing process of epoxy are not releasing water [14].

Epoxy resins however are brittle and have lower resistance toward cracks. Ions such as $H_2O$ and $O_2$ can penetrate into the coating once it cracks. This penetration will allow the corrosion to occur on the surface of the material [15].

### 2.2.3 Coating Failure

There are a few possibilities of coating failures even though coatings are good method to prevent the corrosion. A coating failure happens once coatings no longer work as designed. This failure often occurs because of the weaken of the bond between coating and metal substrate. Surface preparation is very important before applying the coating. The bonding might not occurs or in weak condition due to improper surface preparation. Besides that, during the application of the coating, failure also can cause by environmental factors. Differences in environment temperature, humidity and also cleanliness usually weaken the efficiency of the bond or cause inconsistent spread. Thus, defects such as blistering and cratering may results due to improper surface preparation and inadequate application in environment [16]. Blistering is the formation of round hemispheric pimples on the surface either dry or filled with liquids. Furthermore, for cratering flaws, depressions with small bowl shaped are formed at the coating [11].

Moreover, coating must be applying in a correct way and requires specifics equipment to avoid any failure. Examples of application methods for the coatings are spraying, brushing, dipping, or rolling. Peeling and sagging are the defects that might results due to inadequate application [16]. Detachment and curling of the paint film from the substrates occur in peeling defect due to the loss of adhesion. Besides, the excess downward flow of coatings causes of to gravity which resulting unevenness is called as sagging [11].

Coatings are prone to failure although there are sufficient surface planning, process atmosphere and application method if the coating not correctly formulated. During selection of coating formation, the failure to consider sufficient curing time or temperature involving processing speed and atmosphere results in insufficient curing or interruption of the production process.

Next, mechanical failure that might causes of external impact is also one of the potential failures for coatings. Mechanical failure may result in damage for coating and exposed the surface metal to the environment. Changes in mechanical properties of coatings also causes them vulnerable to cracks micron cracks are very hard to detect and can be difficult to replace [3].

## 2.3 Zinc Oxide

In 1959, idea of nanotechnology was introduced and comprehensive advancement in the field has been made since then. On top of that, Zinc Oxide (ZnO) stand out as one the most useful nanoparticles because of their diverse properties and functionalities. Properties of ZnO nanoparticles are unique physically and chemically. They also are considered as multifunctional material. There are three crystal structure of ZnO as presented in figure 2.6 which are wurtzite, zinc blende and also rocksalt [17]. Zinc oxide can also be classified as a flexible functional material with a range of growth morphologies, such as nanowires, nanorings, nanobelts. The detailed properties of zinc xxide are shown in Table 2.2.

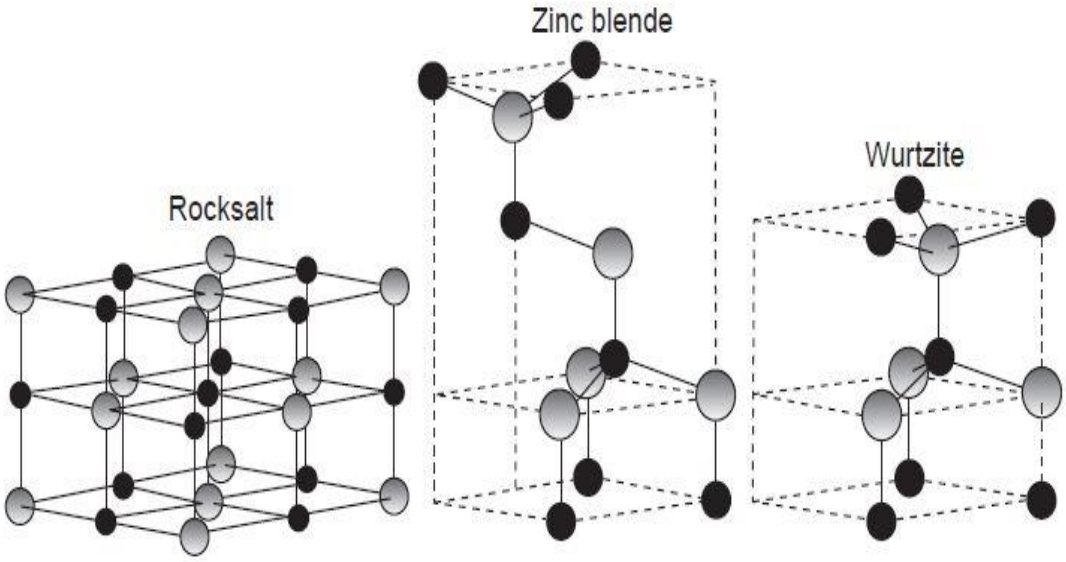



Figure 2. 6: Crystal structures of Zinc Oxide [17]

Moreover, Zinc Oxide also have been used in medical treatment application because of their antibacterial properties. These are also known as free-toxic and also have important mineral elements for the human body. However, inhalation of zinc powder may effect the body condition known as zinc fever, followed by other symptoms such as fever and cough [18]. In addition, zinc oxide nanoparticles are also classified as substance that safe to use by US Food and Drug Administration or known as FDA. Low cost of material for zinc oxide is the another reason for high applications of the nanoparticles in industries [19]. Furthermore, they are commonly used in personal care items, such as cosmetics and sunscreen, due to their high UV absorption properties.

Table 2. 2: Properties of Zinc Oxide

| Properties | ZnO |
|---|---|
| Lattice parameters at 300 K | |
| —$a_0$ (nm) | 0.32495 |
| —$c_0$ (nm) | 0.52069 |
| —$c_0/a_0$ | 1.602(1.633[a]) |
| Density (g/cm$^3$) | 5.606 |
| Stable phase at 300 K | Wurtzite |
| Melting point (°C) | 1975 |
| Thermal conductivity (Wcm$^{-1}$ C$^{-1}$) | 0.6, 1-1.2 |
| Linear expansion coefficient (°C) | $a_0$: 6.5 cm$^3$ × 10$^{-6}$<br>$c_0$: 3.0 cm$^3$ × 10$^{-6}$ |
| Static dielectric constant | 8.656 |
| Refractive index | 2.008 |
| Band gap (RT) | 3.370 eV |
| Band gap (4 K) | 3.437 eV |
| Exciton binding energy (meV) | 60 |
| Electron effective mass | 0.24 |
| Electron Hall mobility at 300 K (cm$^2$/Vs) | 200 |
| Hole effective mass | 0.59 |
| Hole Hall mobility at 300 K (cm$^2$/Vs) | 5–50 |

[a]Value for an ideal hexagonal structures.

Besides that, ZnO also have high surface area to volume ratio. The size of zinc oxide decreases associated with increasing of surface/volume ratios. In particular, zinc oxide with a high surface area to volume ratio are required, however in the absence of any stabiliser, the primary problem is the agglomeration of fine particles precipitated in the solution. Additionally, zinc oxide also are more stable at higher temperature and pressure. Due to its wide band gap of 3.37 eV, strong bond power, and high exciton binding energy (60 meV) at room temperature, Zinc Oxide nanoparticles are an interesting materials for short wave length optoelectronic applications [20].

Next, piezoelectricity is another property of zinc oxide that significant for wide field of application. Oxygen and zinc atoms tetrahedral bond are the starting point for piezoelectricity lies in the crystal structure. The positive and negative charge centres can be disturbed when an external pressure is applied which resulting to a local dipole moment. In addition, Zinc oxide has excelled in the visible spectrum because of its high electrical conductivity and transparency [17].

## 2.4 Smart Coating

A modified of anticorrosive coating known as smart protective coating can actively react by the changes of surrounding environment. Smart coating also responses to any environmental stimulus and change the properties of the metal protected. Nanotechnologies have been used in smart coating or nanocoating to protect the metal from corrode. The widely use of nanotechnologies is because they have interesting chemical and physical properties. Moreover, implementation of nanoparticles in coating formulation nanocoating involves the incorporation of nanoparticles in the coating formulation will improve specific features [21].

Next, nanocontainers can be function as a carrier in coating which controlled the release properties and quickly react with the changes of mechanical properties of the coating and also local environment. The encapsulated corrosion inhibitors or nanocomposites in nanocontainer will release when trigger by corrosion process and protect the surface metal as described in Figure 2.7 [22].

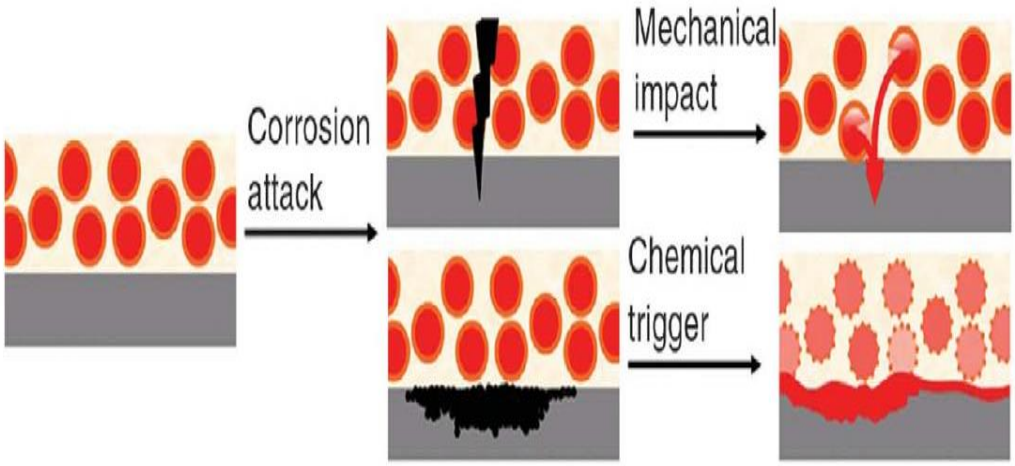



Figure 2. 7: The mechanism of smart coating [22]

There are two various methods to develop smart coating. First, addition inhibitors/nanofillers directly into coatings. Next, inhibitors/nanofillers need to be encapsulate into a carrier before mixed them with the coatings [23]. The term for encapsulate is translated from Latin which give meaning of a little box [24]. The examples of encapsulation can be seen in nature such as egg in sell and a cell in a cell membrane [25].

Materials such as corrosion inhibitors and nanocomposites inside the encapsulation can prevent direct interaction of the materials from the environment. Direct mixing of nanoparticles to the coating will causes undesirable interaction which can effect the protective layer properties of the coating [26]. Moreover, the research carried out by Kartsonakis et al. from proved that it is more effective to encapsulate inhibitors / nanofillers in the coating compared to direct addition approach [27].

Material in the carrier may be released all at the same time or mat be released gradually over time. The control over the encapsulated materials will improve as the size of the carrier reduces. The positive impact of decreasing the size of the carrier has driven the improvement of technology from microcapsules to nano-capsules [24]. Controlling the release rate of the materials in the nanocontainers is the huge advantage for smart coating.

Vacuum method can be conducted to encapsulate the corrosion inhibitors into nanocontainers such as Halloysite Nanotubes (HNT). Figure 2.8 shows the loading methods for Benzotriazole as inhibitor to encapsulate into HNT. Initially, HNT powder need to be mixed into a saturated solution of corrosion inhibitor. Then, vacuum pump will evacuates the precipitate of HNT in the vacuum jar. This step needs to be done in several hours. After that, the sample was then brought back to atmospheric conditions. The process need to be perform for a several cycles in order to increase efficiency of the loading. Afterwards, the solvent was extracted by centrifugation, cleaned with distilled water and dried for a few hours [28].

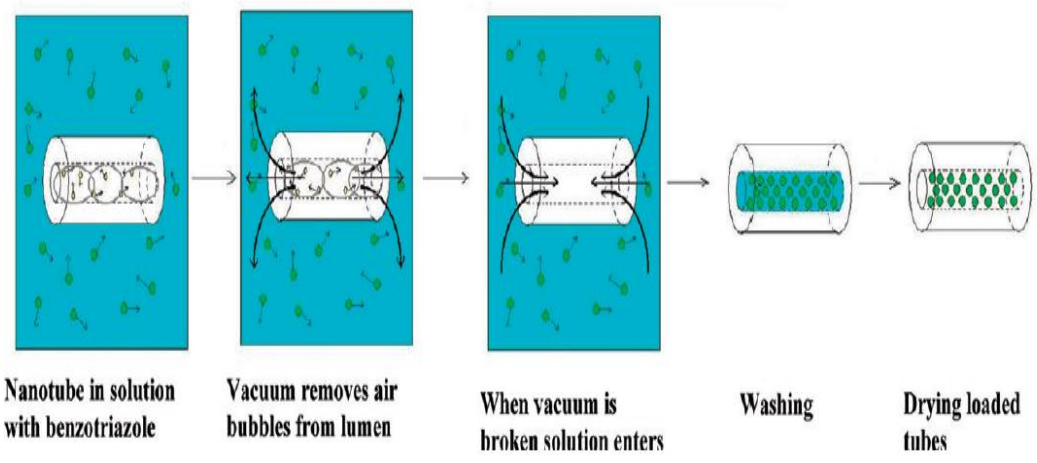



Figure 2. 8: Procedure of loading HNT with Benzotriazole [29]

Change in mechanical action, temperature, pH and pressure may triggered the carriers of the corrosion inhibitors or the nanoparticles [30]. However, mechanical failure might happen other than causes of corrosion prosses and corrosion also not just causes by crack only. Hence, electrochemical potential changes is the most suitable trigger for smart coating [31].

pH also one of the factors that will effects the interaction between nanocontainers and the loaded materials. Change in pH will disturbed the complex stability and trigged the loaded materials to release [32].

## 2.5 Halloysite Nanotubes

Halloysite Nanotubes (HNT) is a mineral 1:1 dioctahedral clay, which is part of the kaolin group. External diameter of HNTs are between 30–190 nm and the internal diameter is approximately 10–100 nm. This morphological data might be different on the other sources [2]. General properties of HNT are presented in Table 2.3.

Table 2. 3: Properties of HNT [33]

| Properties | Detail |
|---|---|
| Chemical Formula | $Al_2(OH)_4Si_2O_5{\cdot}nH_2O$ |
| Length | 0.2–2 μm |
| Outer diameter | 40–70 nm |
| Inner diameter | 10–40 nm |
| Aspet ratio (L/D) | 10–50 |
| Elastic modulus (theoretical value) | 140 GPa (230–340 GPa) |
| Mean particle size in aqueous solution | 143 nm |
| Particle size range in aqueous solution | 50–400 nm |
| BET surface area | 22.1–81.6 $m^2/g$ |
| Pore space | 14–46.8% |
| Lumen space | 11–39% |
| Density | 2.14–2.59 $g/cm^3$ |
| Average pore size | 79.7–100.2 Å |
| Structural water release temperature | 400–600 °C |

Moreover, HNTs are naturally occurring eco-friendly nanotube that is harmless to humans and the trendsetter for green technology [34]. HNT is chemically similar to kaolinite, but HNT layers are separated by a water layer ($H_2O$). Therefore, the chemical formula of HNT is $Al_2(OH)_4Si_2O_5 \cdot nH_2O$. The structure of halloysite particles are shown in figure 2.9. The lumen in HNTs makes them capable of carrying drugs and agents to be used as nanocontainers for many applications such as sustained-release drug delivery [38]. Many types of active agents can be encapsulated that serve as nanofillers inside inner cavity of HNTs and combined with invalid spaces of the multi-layer aluminosilicate shells of HNTs [35].

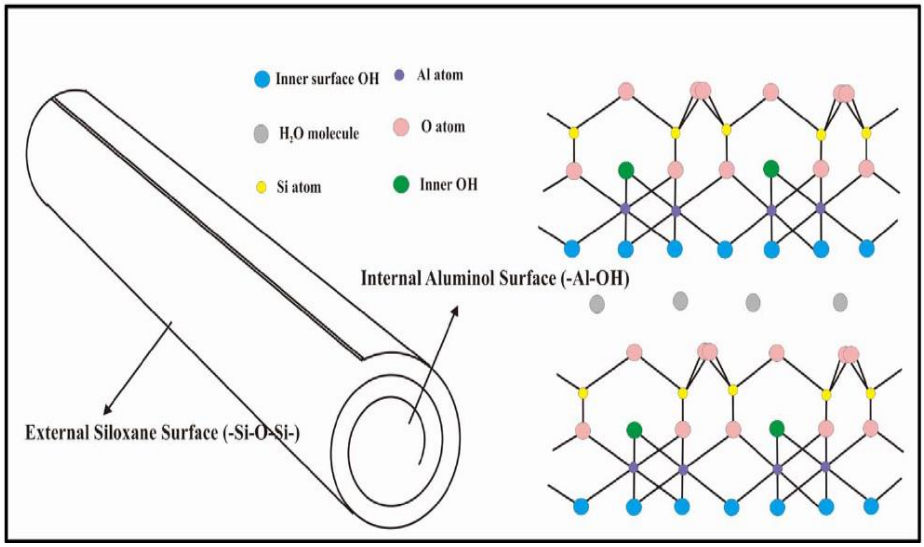



Figure 2. 9: Structure of Halloysite Particle.

Additionally, halloysite nanotubes are strong biocompatible materials and very minimal toxicity. Therefore, it is safe to use in different fields. Besides, HNT is chemically stable with an estimated length of 0.5–1 μm [60]. The outer surface is hydrophilic because of the chemical bonds in the HNT structure whereas the inner lumen is hydrophobic. In general, with an adequate pre-treatment, HNT can load and release both the hydrophilic and hydrophobic compounds. The micrographs of HNTs are elucidated in Figure 2.10.

Furthermore, HNT is only for $4 per kg which is far more cheaper than carbon nanotube (CNT) that can be obtain with the price of $500 per kg. Beside that, HNT also is easy to obtain and widely used due to their high availability in markets [2].

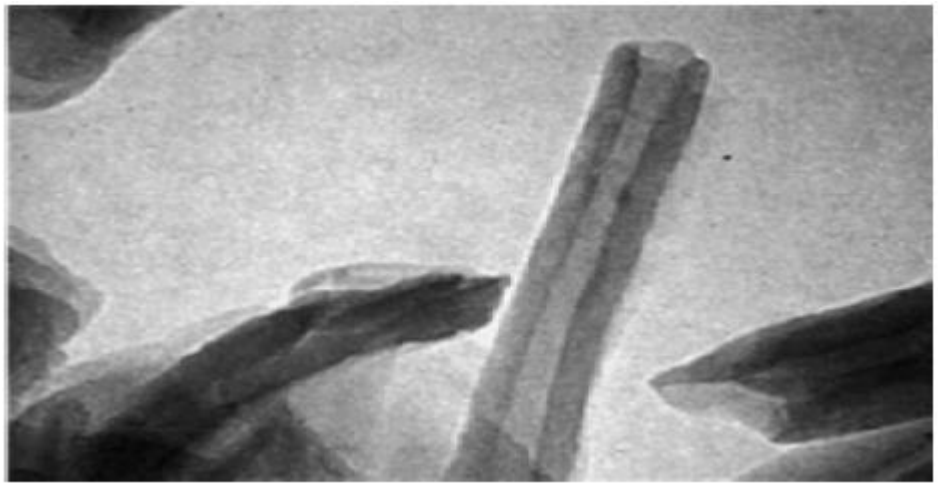


Figure 2. 10: TEM micrograph of HNTs [35]

# CHAPTER 3

# METHODOLOGY

## 3.1 Project Flowchart

Figure 3.1 represents the flowchart of this project.

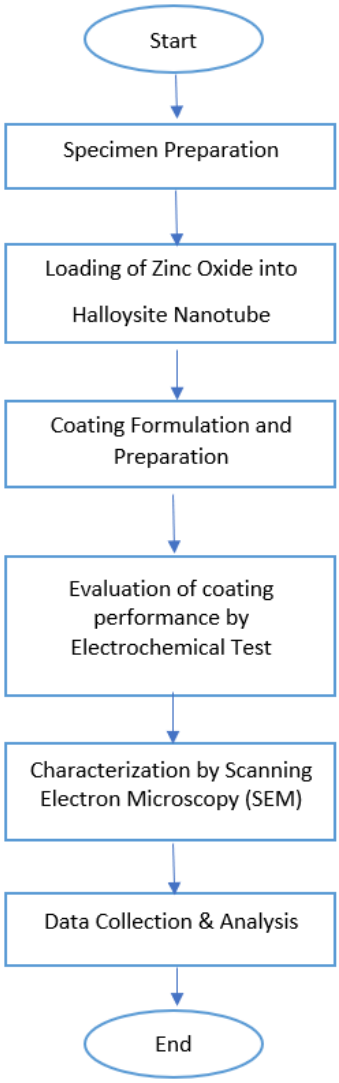



Figure 3. 1: Project Flowchart for FYP 1 and FYP 2

## 3.2 Experiment Setup

### 3.2.1 Specimens Preparation

A106 Carbon Steel was used as tested metal in this study. The metal was cut precisely into a few pieces by the dimension of 1cmx1cm as shown in figure 3.2.

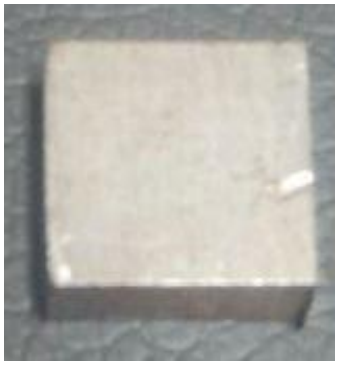


Figure 3. 2: Specimen substrate of A106 Carbon Steel

Then, the metal substrates were drilled using drilling machine as shown in figure 3.3. The metals were drilled to create small hole so the copper wires can be connected and soldered to the metal substrates as shown in Figure 3.4(a) to have an electrical connection. Next, metal specimens were mounted by using epoxy resin as shown in Figure 3.4(b). Hardener was added to epoxy coating with the ratio 4.4:1 of epoxy resin to hardener. The mixture was mixed carefully to avoid the formation of bubbles until the mixture became transparent.

Figure 3. 3: Drilling Machine

The release agent was applied to the internal side of the mould before adding the mixture to avoid the epoxy from sticking to the mould when released. Next, at room temperature, mounted samples were cured for 24 hours as shown in figure 5. All samples were grinded using sandpapers (Sic) started from grade 60, 120, 240, 320, 400 and lastly 600 as per ASTM D6943 standards as illustrated in Figure 3.4(c). Figure 3.4(d) shows the prepared sample after grinding process.

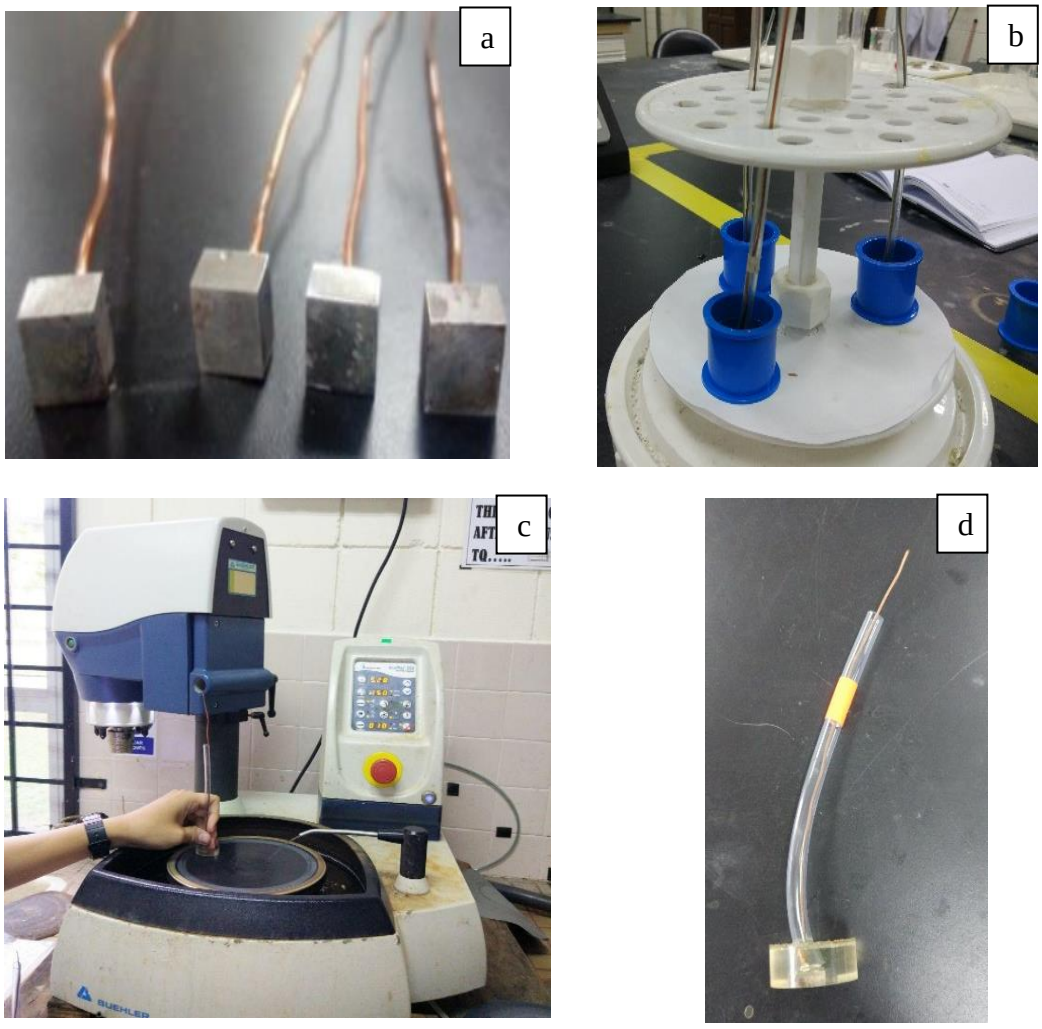



Figure 3. 4: Steps for Sample Preparation; (a) Soldered Sample, (b) Mounting Process, (c)Grinding Process, and (d) Prepared Sample

### 3.2.2 Loading of Zinc Oxide into HNT

Zinc oxide as shown in Figure 3.5 was loaded in HNT. 2.5grams of ZnO was dissolved in 2.5ml of ethanol and stirred by magnetic stirrer on the hot plate for 1 hour at 350rpm as shown in figure 3.6(a). Then, 3 grams of HNT was mixed with the solution before stirring them for 24 hours in room temperature. Ratio of ZnO to HNT used in this project was 5:6, as referred to previous study [28]. Next, the solution was transferred to a rotary evaporator. Vacuum at 175 mbar, rotation speed of 150 rpm and water bath temperature of 60°C were applied to load ZnO into lumen of HNT. Figure 3.6(b) shows the loading process by the rotary evaporator. In addition, the process of the above need to be complete in 4 cycles for a complete evacuation process and washed 3 times using distilled water to eliminate the residue of ZnO. The compound was then heated at 50°C in the oven for 24 hours to abolish the remaining solvent as shown in figure 3.6(c). The methods of ZnO into HNT was adapted from previous study [28]. Figure 3.6(d) showed the result from the drying process using the oven.

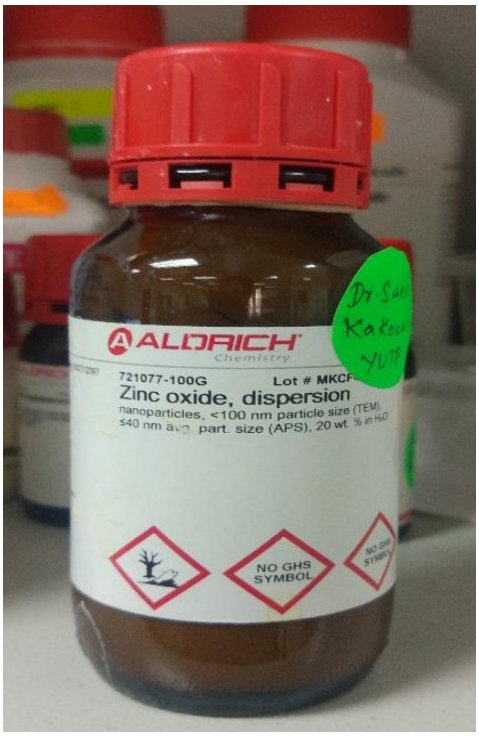



Figure 3. 5: Zinc Oxide

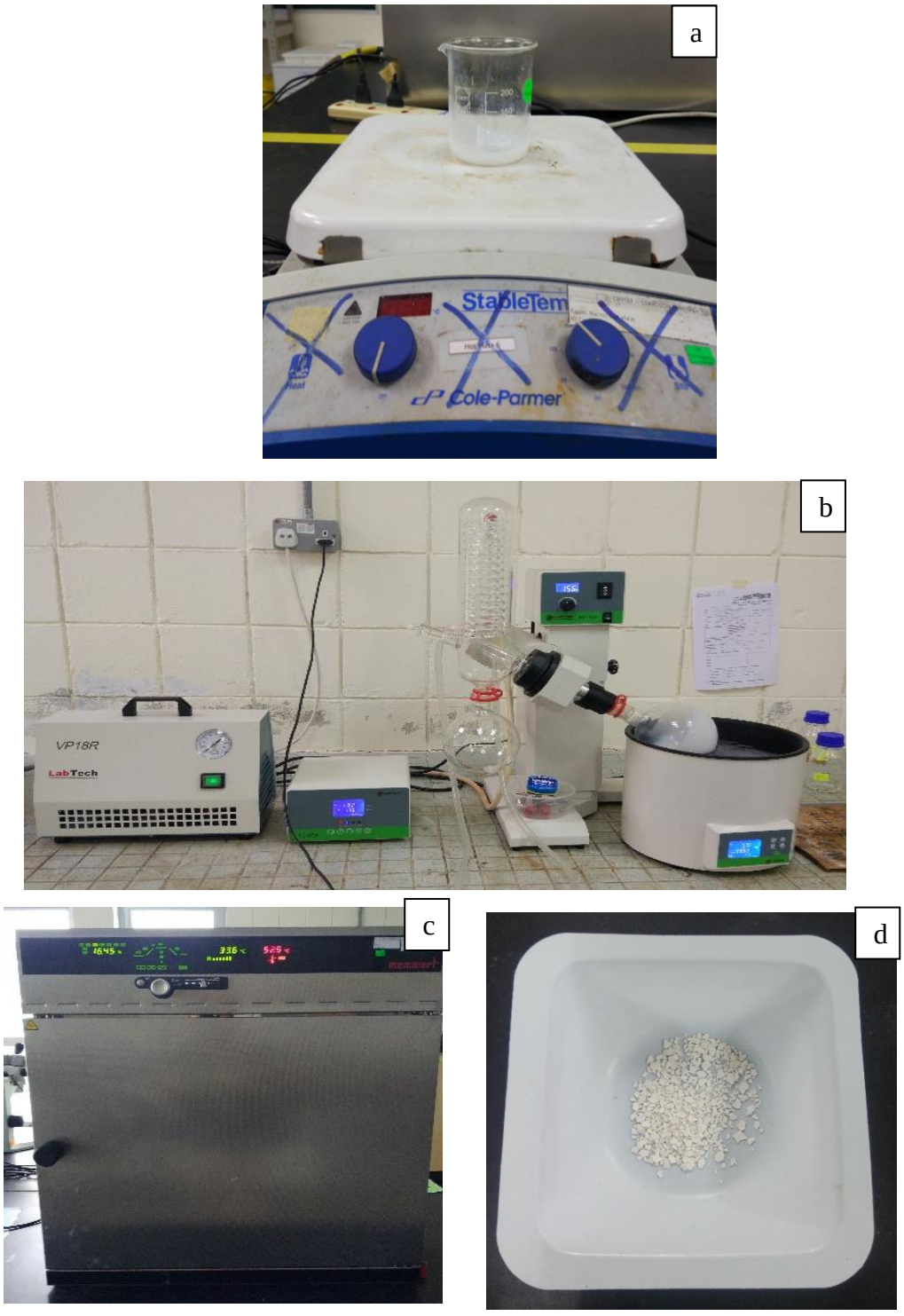



Figure 3. 6: Process of loading ZnO into HNT; (a) The mixing process (a) The Vacuum Process, (b) The Drying Process, and (c) The Prepared Sample

### 3.2.3 Coating Preparation

ZnO-loaded HNT with different concentration of 1wt%, 5wt% and 10wt% and labelled as CEP1 , CEP5, CEP10 was added to the coating materials. Epoxy resin, EPIKOTE 828 that mixed with the hardener, LS-D308 as shown in figure 3.7 have been used as the coating materials.


Figure 3. 7: Main materials used for coating (a) Epoxy Resin EPIKOTE 828 (b)Hardener LS-D308

Moreover, the coating containing 100wt% of epoxy resin mixed with hardener labelled as EP was formulated to be use as the comparison to the modified coating that contains ZnO-loaded HNT (CEP1, CEP5, CEP10). The test matrix of this study is described respectively in Table 3.1.

Table 3. 1: Test Matrix

| Sample Code | ZnO loaded HNT | Epoxy + Harderner |
|---|---|---|
| EP | - | 100 wt% |
| CEP1 | 1 wt% | 99 wt% |
| CEP5 | 5 wt% | 95 wt% |
| CEP10 | 10 wt% | 90 wt% |

The weight of the filler was calculated by using Equation 3.1. The weight ratio of 1:2 of epoxy to hardener have been used. All the materials including ZnO-loaded HNT, epoxy resin and hardener were weighted by using electronic balance as shown in figure 3.8.

Figure 3. 8: Electronic Balance

In order to ensure the particles are dispersed and to avoid agglomeration, ZnO-loaded HNT was mixed in acetone. The solution was stirred for 30 minutes at 350rpm to obtain a uniform dispersion. Then, 2 grams of epoxy, EPIKOTE 828 was added to the mixture and stirred for 5 hours at 80°C using hot plate as shown in figure 3.9. This step is important to allow dispersion of ZnO-loaded HNT in epoxy resin.

After that, 1 gram of hardener, LS-D308, was manually mixed with the weight ratio of 1:2 to the epoxy. The procedures for preparation of the coatings was referred from past research [28]. The modified coating was applied to a grinded specimen by using a brush. Dry film thickness (DFT) was used to control the thickness of the coating for each specimen. The thickness was controlled to be at 230 μm to 280 μm. The procedures were repeated for CEP1, CEP5 and CEP10. For EP, epoxy resin were manually mixed with hardener by ratio of 2:1 and applied to the specimens.

$$W = \frac{x\,(E + H)}{(1 - x)}$$ (Equation 3.1)

$W$ : Weight of the filler‘s (ZnO loaded HNT)

$x$ : Mass fraction of the filler to the total mass of epoxy and hardener

$E$ : Mass of epoxy

$H$ : Mass of hardener


Figure 3. 9: Mixing process of ZnO-loaded HNT on hot plate

### 3.2.4 Solution Preparation

30 grams of NaCl was dissolved in 1 litre distilled water by using glass rod to prepare for 3.0wt% NaCl solution. This solution was used in the electrochemical test.

### 3.3 Electrochemical Testing

The electrochemical testing namely Electrochemical Impedance Spectroscopy(EIS) was conducted to find out the coating performance of all the specimens. ACM Instrument Gill 12 Weld as shown in figure 3.10 was used to record and analyse EIS data. Moreover, EIS was run by using three electrodes cell which are Ag/AgCl as the reference electrode, the sample as the working electrode, and the stainless steel as the counter electrode or auxiliary electrode. The electrochemical set up in glass cell is as shown in Figure 3.11. The amplitude and the frequency for EIS test were set at 20 mV and 100 kHz to 0.1 Hz, respectively.

In this experiment, all the specimens (EP, CEP1, CEP5 and CEP10) were immersed for 15days in 3.0wt% of NaCl [36]. EIS measurements were collected at day 1 followed by 3, 5,10 and 15 days of immersion.

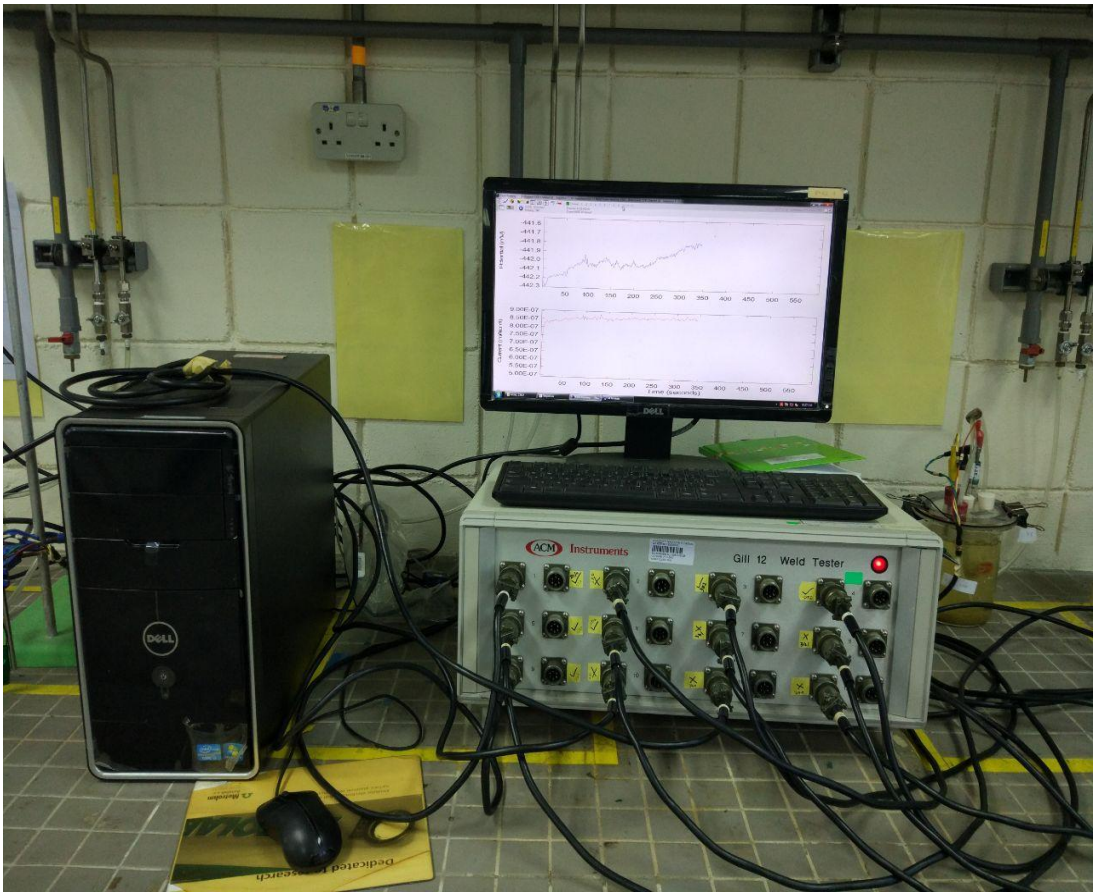



Figure 3. 10: Autolab potentiostat/galvanostat instrument

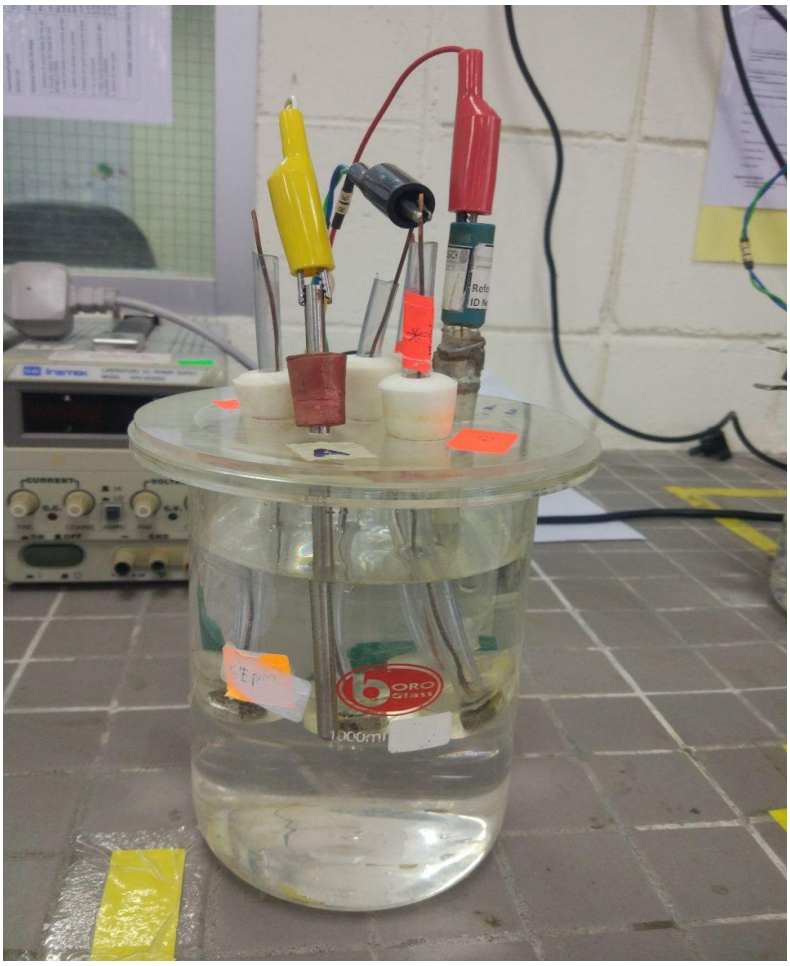


Figure 3. 11: Glass Cell Set Up for Electrochemical Testing

### 3.4 Scanning Electron Microscopy (SEM)

Surface morphologies of the all specimens were investigated by using Scanning Electron Microscopy (SEM) as shown in Figure 3.12. Electron beam is being used in SEM instead of the light beam. The electron beam that is applied to the sample being examined is fired at the top of the machine, from the electron gun. The information provided by the electron receiver is transformed into a 3D diagram image [37][38].

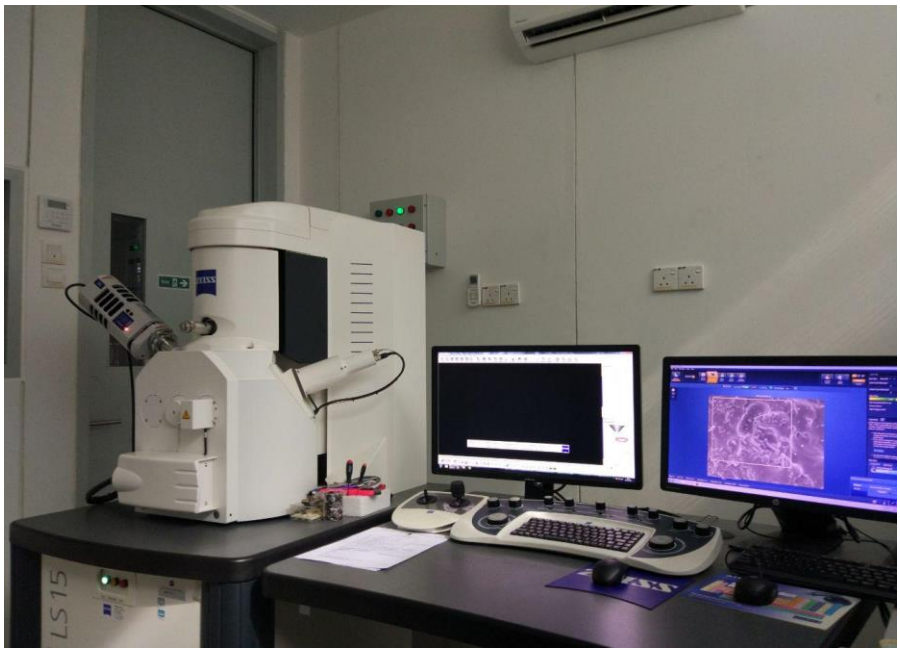



Figure 3. 12: Scanning Electron Microscope (SEM)

## 3.5 Gantt Chart and Key Milestone

Milestone Plans and Gantt Charts are simple and good for project planning and practice methods used for project development.

### 3.5.1 Gantt Chart

The scheduling of the project for FYP 1 is visualized in Table 3.2 to show the planned duration for each project task.

Table 3. 2: Gantt Chart for FYP 1

| PROJECT TASKS | Weeks | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
| Finalization of project title with supervisor | ■ | | | | | | | | | | | | | |
| Critical Literature Review on related topic | | ■ | ■ | ■ | ■ | ■ | | | | | | | | |
| Material acquisition | | | ▲ | ■ | | | | | | | | | | |
| Preparation of interim report & proposal defence | | | | ■ | ■ | ■ | ■ | | | | | | | |
| Proposal Defence | | | | | | | | ■ | ■ | | | | | |
| Preparation of interim report | | | | | | | | | | ■ | ■ | ■ | ■ | |
| Submission of interim report | | | | | | | | | | | | | | ■ |

| | |
|---|---|
| ■ | Process |
| ▲ | Key Milestone |

The scheduling of the project for FYP 2 is visualized in Table 3.3 to show the planned duration for each project task.

Table 3. 3: Gantt Chart for FYP 1

| PROJECT TASKS | Weeks | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
| Specimen Preparation | ■ | ■ | | | | | | | | | | | | |
| Coating Preparation | | | ■ | ■ | | | | | | | | | | |
| Electrochemical Test Experiment | | | | | ▲ | ■ | ■ | ■ | | | | | | |
| Characterization of coating | | | | | | | | ■ | ▲ | | | | | |
| Data Collection and Analysis | | | | | | ▲ | ■ | ■ | ■ | | | | | |
| Submission of Progress Report | | | | | | | ■ | | | | | | | |
| Pre-SEDEX | | | | | | | | | | ■ | | | | |
| Submission of Draft Final Report | | | | | | | | | | | ■ | | | |
| Submission of dissertation (soft copy) | | | | | | | | | | | | ■ | | |
| Submission of technical paper | | | | | | | | | | | | ■ | | |
| Viva | | | | | | | | | | | | | ■ | ■ |
| Submission of project dissertation (Hard Bound) | | | | | | | | | | | | | | ■ |

| | |
|---|---|
| ■ | Process |
| ▲ | Key Milestone |

### 3.5.2 Key Milestones

All key milestones in FYP 1 and FYP 2 are shown in Table 3.4 and Table 3.5 respectively.

Table 3. 4: Key Milestones in FYP 1

| Week | Milestone |
|---|---|
| 3 | Material acquisition |

Table 3. 5: Key Milestones in FYP 2

| Week | Milestone |
|---|---|
| 5 | Electrochemical Test Experiment |
| 6 | Characterization of coating |
| 9 | Data Collection and Analysis |

# CHAPTER 4

# RESULT AND DISCUSSION

All results and some discussions on the performance of the modified coatings are showed in this chapter. The electrochemical test known as EIS was employed while SEM was conducted to relate the surface structure of tested samples. The results from the electrochemical test will be presented mostly by plotted graph and the analysis will be conducted by investigating the behaviour of the graph.

## 4.1 Electrochemical Test

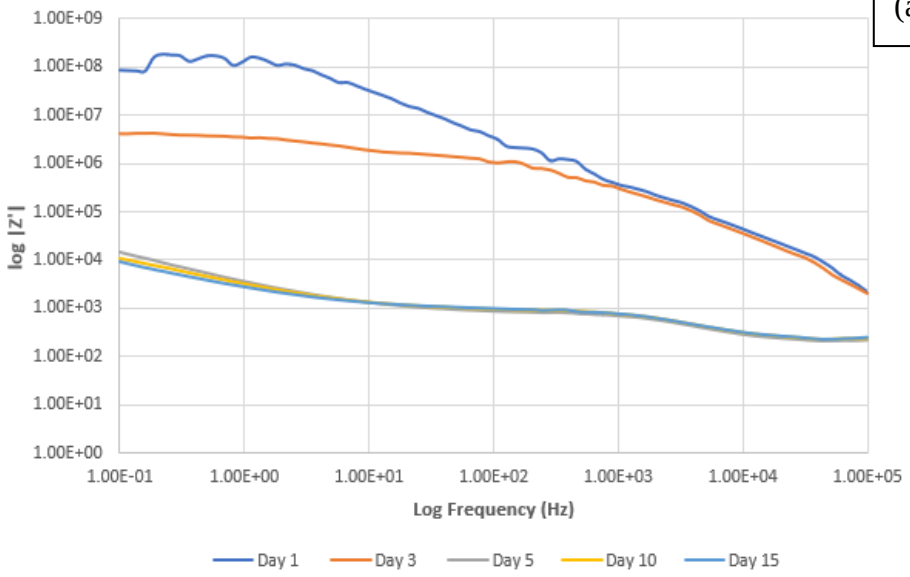
Electrochemical Impedance Spectroscopy (EIS) was deployed as the electrochemical test for all coating system. EIS has been recorded for 15 days of immersion for coatings at day 1, day 3, day 5, day 10 and day 15. EIS methods can be presented in the form of Bode plot and also Nyquist plot to interpret the data.

### 4.1.1 Bode Blot

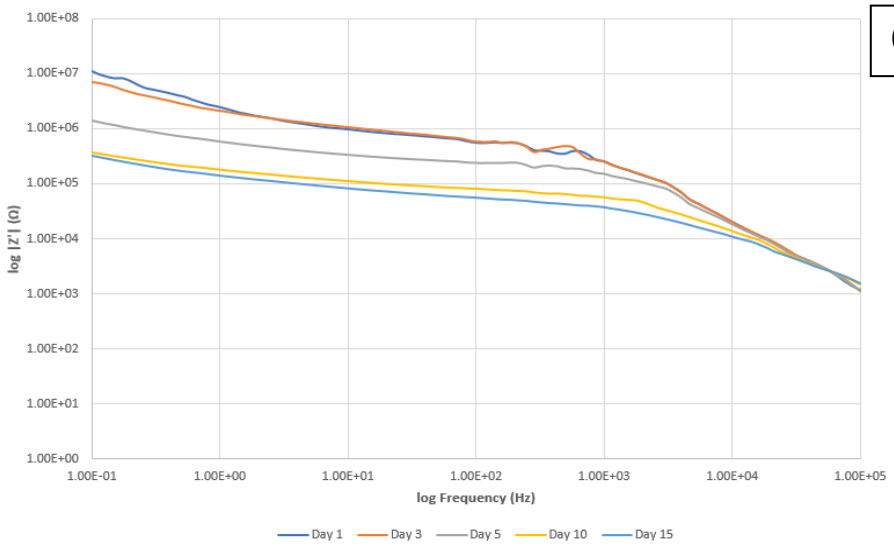
Bode plot was plotted based on impedance values (Z‘) and also frequency dependence. Figure 4.1 shows Bode plot for EP, CEP1, CEP5 and CEP10 coatings after 15 days of immersion. Range impedance values from frequency of 100kHz until 0.1Hz can be observed from the graph. High frequency in a coating system is related to the coating properties which also indicate the solution resistance. In contrast, coating system with low frequency is correlated with the corrosion process happened on the metal surface or the interface between metal and coating. It also can be described as the coating performance [39]. From Bode plot, EP coating plotted higher than other graphs as shown in Figure 4.14 (a) after 1 and 3 days of immersion. The impedance range was around $10^6 – 10^7$ Ω at low frequency and around $10^3$ Ω at high frequency. Moreover, Bode plot of neat epoxy, EP significantly dropped after 3 days of immersion reflecting the decreasing in coating performance.

Figure 4.14 (b), (c), and (d) present Bode plot curves of CEP1, CEP5, and CEP10 coating, respectively. It can be seen from Bode plot of the modified coatings, CEP1, CEP5, and CEP10 that at high frequency, the impedance values obtained were around $10^3$ Ω. The impedance values were in a similar range which was indicating that almost similar solution resistance was observed by increasing the immersion time. However, coating performance can be represented by the impedance value at low frequency. Bode plot of modified coatings (CEP1, CEP5, and CEP10) were initially decreased after 3 days of immersion due to the corrosive ion that started to penetrate into the coating system. Further explanation of the changes in the impedance value at low frequency (0.1Hz) as a representative to coating protection properties is elaborated in the next section.

(a)




(b)



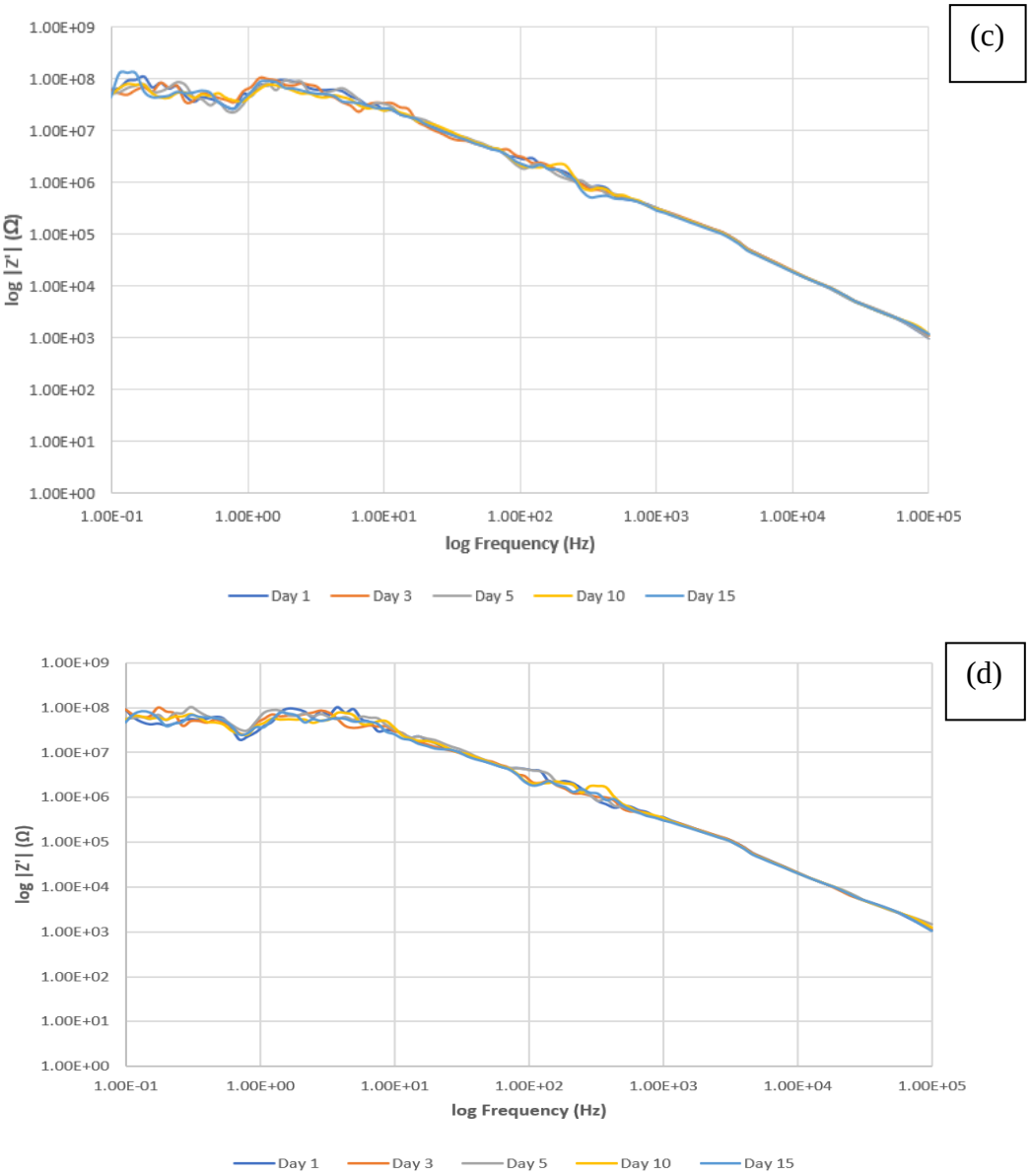



Figure 4. 1: Bode Plot of (a) EP, (b) CEP1, (c) CEP5, (d) CEP10

|Z'|0.1Hz indicates the impedance values at 0.1Hz demonstrate the impedance values at the low frequency. It could also be taken as the protective properties of the coating [41]. The |Z'|0.1Hz values corresponded to time of immersion are shown in Figure 4.2.

Coating with |Z'|0.1Hz value > $10^8$ Ω can be considered as a coating with excellent barrier properties [40]. However, coating with |Z'|0.1Hz value > $10^6$ Ω could be categorised as a good coating, while |Z'|0.1Hz value < $10^6$ Ω was exhibited as poor protection coating. At day 1 of immersion, it can be seen that all the coating system obtained high |Z'|0.1Hz value which was 8.37E+07 Ω, 1.089E+07 Ω, 6.133E+07 Ω,

and 9.037E+07 Ω for EP, CEP1, CEP5 and CEP10, respectively. Those values indicated that all the coating systems had high protection ability and could act as a good barrier in prohibiting diffusion of water, oxygen molecules, or chloride ions from the electrolyte solution. Those molecules may reach the metal surface and caused corrosion. However, the coating performance cannot be compared based on the result of the initial time of immersion. At the initial time of immersion, the coating system is flawless and no degradation occurred [41].

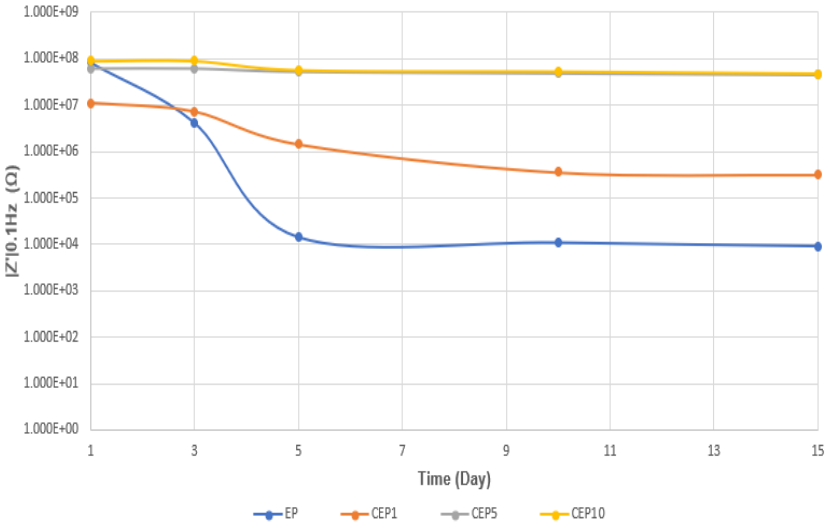



Figure 4. 2: |Z'|0.1Hz value of Time-Dependence for EP, CEP1, CEP5 and CEP10 coatings

After immersed for 3 days, the |Z'|0.1Hz value of EP coating decreased quickly to 4.236E+06 Ω due to the diffusion of electrolyte solution into the coating system. Then, the coating system failed in protecting the metal substrate after 5 days immersed in 3.0wt% NaCl which could be seen from the significantly decrease value of |Z'|0.1Hz to 1.439E+04 Ω. It shows that the coating protection ability failed to provide proper protection for the metal substrate, since for |Z'|0.1Hz < $10^6$ Ω is associated to the poor anticorrosive protection of the coating. The |Z'|0.1Hz value continues to decrease after 10 days of immersion to 1.095E+04 Ω. The impedance continuously dropped to 9.209E+03 Ω after 15 days of immersion. It reflects the continuous penetration of the electrolyte solution into the coating system.

Generally, the graphs for modified coatings show a same pattern of EP coating where the impedance values decreased with time. However, it was discovered that the impedance values of the modified epoxy coatings (CEP1, CEP5 and CEP10) were greater than neat epoxy (EP) that might be contributed to the existence of ZnO-loaded HNT as the fillers [42]. At the initial duration of immersion, the impedance value of modified coatings (CEP1, CEP5 and CEP10) represents an excellent coating system as mentioned above. After 3 days of immersion, the values decreased to 7.121E+06 Ω, 6.143E+07 Ω and 9.101E+07 Ω for CEP1, CEP5 and CEP10 respectively. The impedance values were slightly decreased after 5 days to 1.428E+06 Ω, 5.263E+07 Ω and 5.634E+07 Ω. After 10 days, the |Z'|0.1Hz values recorded are 3.608E+05 Ω , 4.856E+07 Ω and 5.235E+07 Ω for CEP1, CEP5 and CEP10 respectively. At the time of immersion, CEP1 coating failed to serve as an excellent protection due to the value recorded is less than $10^6$. CEP1 failed to provide an excellent protection after 15 days of immersion where the value obtained was 3.199E+05 Ω. It might due to the diffusion of electrolyte solution [42]. Meanwhile, the |Z'|0.1Hz value of CEP5 and CEP10 after 15 days of immersion show an almost stable value. The values were 4.516E+07 Ω and 4.727E+07 Ω for CEP5 and CEP10, indicating that the coatings provided good corrosion protection to the metal after 15 days of immersion.

The modified and unmodified epoxy coatings show a similar trend of |Z'|0.1Hz values corresponded to time which prolonged in the immersion time causing the decreasing of impedance value. This might be due to the diffusion of water, oxygen, and ionic molecules into the coating barrier. Initially, the electrolytes penetrate through the coating layer and constructed pathways through the coating in various depths [42]. However, the |Z'|0.1Hz value of modified epoxy (CEP1,CEP5,CEP10) was higher and more stable than neat epoxy (EP). It was associated with the presence ZnO-loaded HNT.

The existence of nanofillers could increase the anti-corrosive properties of the coating. When the electrolyte solution penetrates into the coating system, it sets the path at various depths. Nanofillers can create winding pathway for the water and other corrosive species penetration. Thus, the presence of nanofillers could decrease water uptake occurred in the coating which resulted in the enhancement of barrier properties of the coating [43]. Higher corrosion resistance of CHEP10 and CHEP5 compared to EP could be attributed to the OH bonding between the nanotube and epoxy coating

[42]. Furthermore, it can be observed that coating with 1 wt% ZnO-loaded HNT into the coating system exhibits lower corrosion protection than 10 wt% concentration of ZnO-loaded HNT. For further investigation, Nyquist Plot of EIS data will be elaborated.

### 4.1.2 Nyquist Plot

In Nyquist plot, impedance of real values was plotted against the imaginary values. Data of EIS were interpreted by an electrical equivalent circuit including resistor, capacitance and seldom constant phase element (CPE) [40]. At the day 1 of immersion, all coating systems either modified epoxy coatings (CEP1, CEP5, CEP10) or neat epoxy coating (EP), both show excellent coating properties. At this time, an equivalent electrical circuit shown in Figure 4.13(a) is used to fit the impedance data. The coating capacitance (Cc) in the circuit was arranged in parallel to the coating resistance (Rc) and in series to the solution resistance (Rs) [44]. From this figure, it can be seen that the real and imaginary impedance spectra were represented by one semicircle. Initially, the comparison of the coating resistance can be observed from the size of the semicircle. Figure 4.4 shows that the EP coating revealed the biggest size of semicircle reflecting the highest coating resistance of 1.35E+08 Ω, followed by CEP10, CEP5 and CEP1 at 4.81E+07, 1.90E+07 and 3.94E+07, respectively.

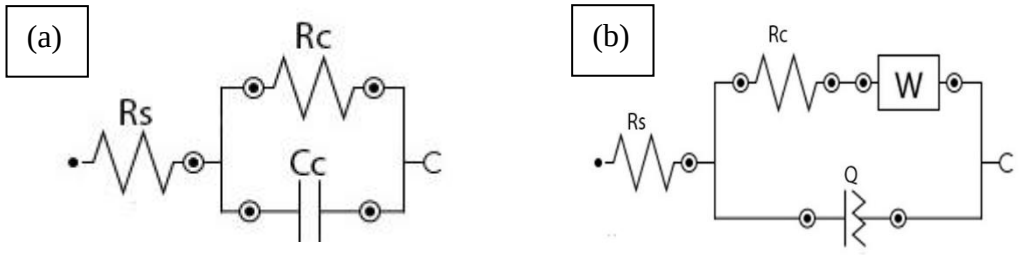



Figure 4. 3: Equivalent Electrical Circuit (a) [R(RC)] (b) [R([RW]Q)]

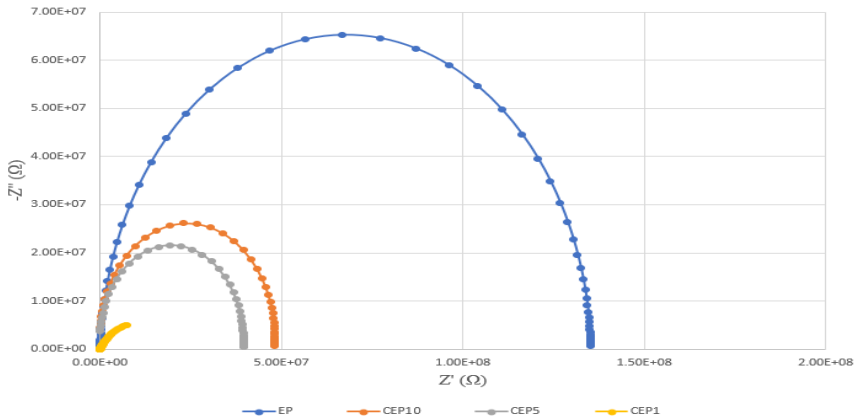



Figure 4. 4: Nyquist Plot for EP, CEP1, CEP5 and CEP10 after 1 day of immersion

At the initial duration of immersion, all coatings either neat or modified epoxy coatings, revealed one time constant of Nyquist plot. Thus, the plots were well fitted to model circuit of [R([RW]Q)] as illustrated in Figure 4.3 (b). By increasing the immersion time, a straight line or small tail in Nyquist plot was produced at low-frequency region. The straight line or tail in Nyquist plot corresponded to the diffusive Warburg impedance at the low-frequency region. This indicates the continuously decreasing of anticorrosive capability that took place in the diffusion control process in the coating system [45]. It could be related to the diffusion process of water, oxygen, or electrolyte molecules in the coating system [42].

Warburg coefficient indicates the measurement of the direct ion diffusion of the corrosive species through the coating system. Warburg coefficient was indicated to the water uptake in the coating system since the formation of a chemical potential was enable by that element. The enhancement of the Warburg coefficient deals with the water uptake. The reduction in Warburg coefficient is related to the enhancement of pore or the coating resistance due to the role of the coating's filler [46].

Warburg values of EP coating increased continuously by increasing the immersion duration from 1.28E-06 Mho at day 3 to 1.78E-04, 1.30E-04 and 1.48E-04 Mho after 5, 10 and 15 days of immersion. Moreover, the coating protection performance can be investigated from the coating resistance and the coating capacitance. The reduction of coating resistance (Rc) and the increasing of coating capacitance (Cc) indicate the continuation of coating degradation. Nyquist plot for EP coating is shown in Figure 4.5.

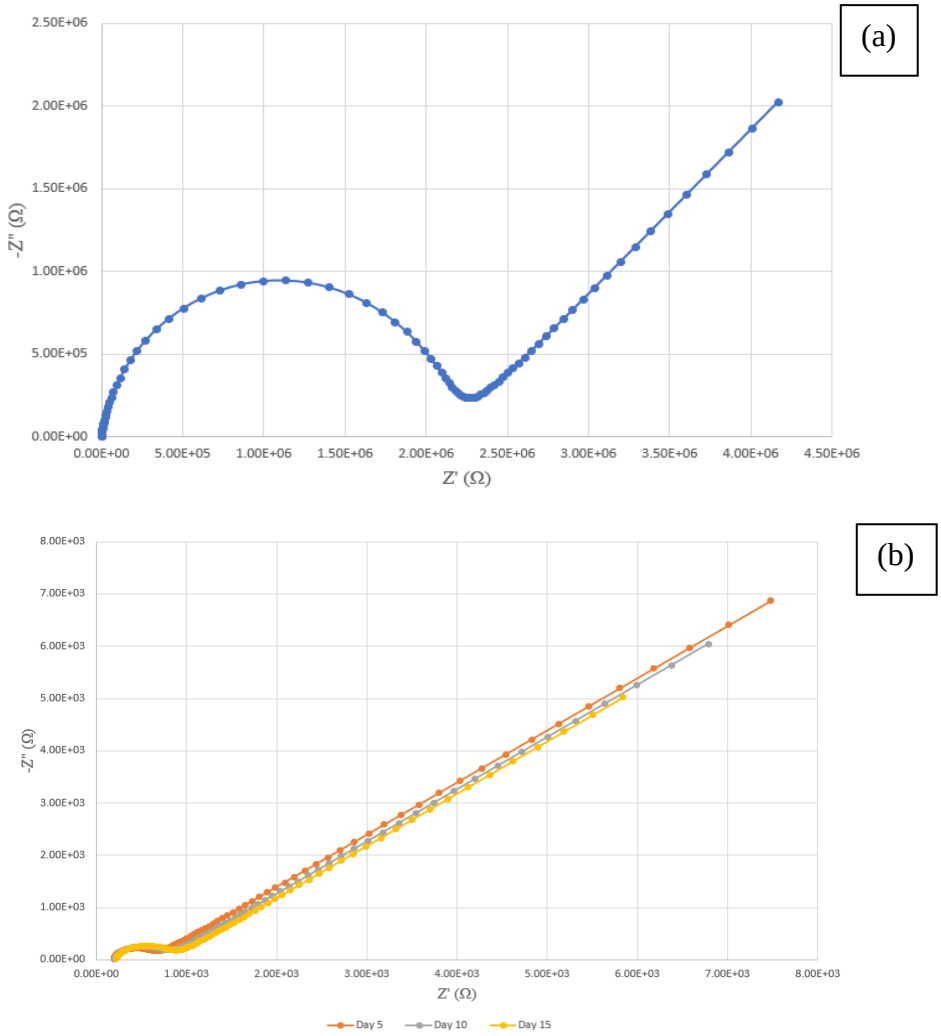
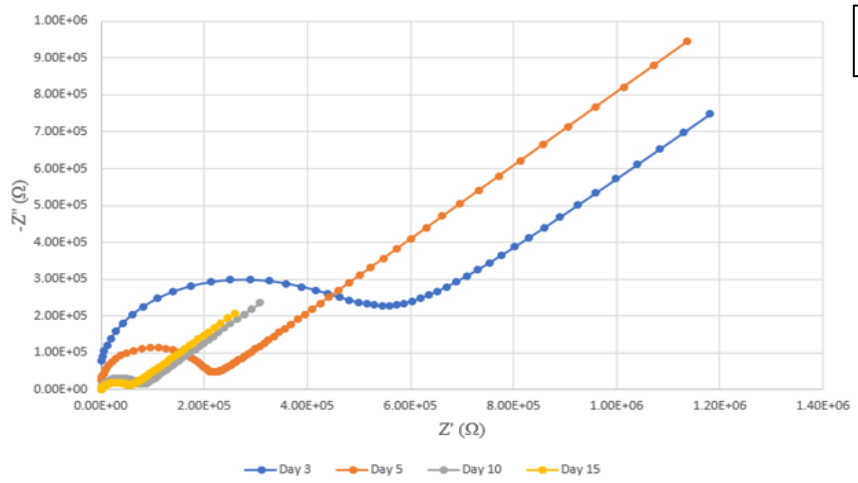



Figure 4. 5: Nyquist Plot for EP (a)After 3 days (b) 5-15 days of immersion

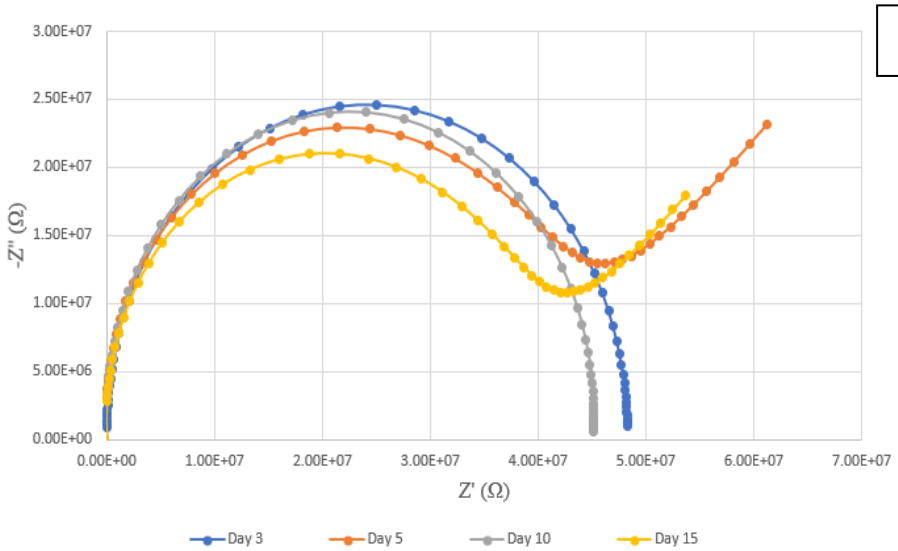
Meanwhile, the Warburg values of CEP1 was reduced from 4.30E-06 Mho to 3.79E-06 and 2.3E-07 Mho after 3, 5, 10 days of immersion. The Warburg value after 15 days of immersion however increase to 9.44E-07 Mho. Besides that, Warburg value for CEP5 coating tends to decrease as time elapsed from 5.23E-08 Mho after 3 days of immersion to 2.51E-08 Mho after 15 days. Moreover, CEP10 coating also provided a reduction in Warburg impedance values which were 6.58E-08, 5.26E-08, 3.39E-08 and 3.35E-08 Mho after 3, 5, 10 and 15 immersion days. Besides, all the modified coatings exhibit the reduction of the resistance values (Rc) and the increasing of capacitance (Cc) values indicating that the corrosive species and water uptake occurred in the coating system continuously. Nyquist Plot for modifies epoxy coatings are shown in Figure 4.6.

Furthermore, at CEP10, the EIS results showed that the resistance values slightly increased after 10 days of immersion. The values increase from 4.55E+07 Ω to 4.76E+07 after 10 and 15 days of immersion as shown in Table 4.1. It was an indication that the development of coating protection of modified epoxy that might be due to the presence of ZnO-loaded HNT. In addition, from the Nyquist plot, equivalent electrical circuit, and electrical elements value, it can be observed that the modified epoxy produced an improved corrosion protection compared to the neat epoxy coating. Incredibly the best corrosion protection was obtained for the coatings with 10 wt.% of nanofillers. CEP10 was observed as well as barrier protection due to improved connectivity within pigments and less void volumes [47]. Thus, modified coatings (CEP1, CEP5 and CEP10) showed to have some improvement on corrosion protection compare to neat epoxy coating (EP).

(a)




(b)



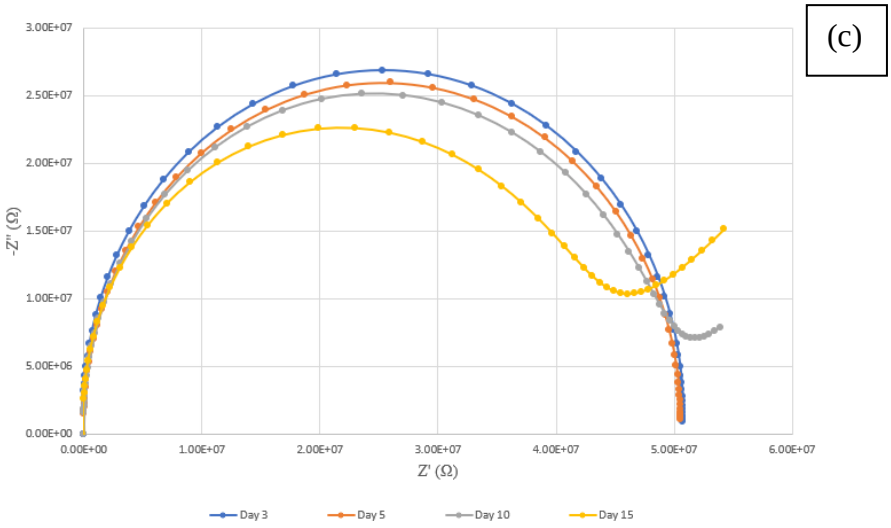



Figure 4. 6: Nyquist Plot for modified coatings after 3,5,10, and 15 days of immersion (a)CEP1 (b)CEP5 (c)CEP10

Table 4. 1 : EEC Values for EP, CEP1, CEP5 and CEP10

| **Specimens** | **Immersion time (Day)** | **Rc (Ω)** | **Cc (F)** | **W ($Mh_0$)** |
|---|---|---|---|---|
| **EP** | Day 3 | 2.15E+06 | 1.54E-09 | 1.28E-06 |
| | Day 5 | 6.23E+02 | 1.3939-07 | 1.30E-04 |
| | Day 10 | 5.46E+02 | 2.24E-07 | 1.48E-04 |
| | Day 15 | 4.25E+02 | 3.63E-07 | 1.78E-04 |
| **CEP1** | Day 3 | 4.51E+05 | 2.51E-10 | 4.30E-06 |
| | Day 5 | 1.92E+05 | 3.44E-10 | 3.79E-06 |
| | Day 10 | 7.37E+04 | 4.39E-09 | 2.10E-07 |
| | Day 15 | 5.41E+04 | 2.04E-08 | 9.44E-07 |
| **CEP5** | Day 3 | 4.83E+07 | 7.04E-10 | 5.23E-08 |
| | Day 5 | 4.51E+07 | 4.98E-10 | 4.02E-08 |
| | Day 10 | 3.97E+07 | 4.39E-10 | 2.94E-08 |
| | Day 15 | 3.71E+07 | 5.57E-10 | 2.51E-08 |
| **CEP10** | Day 3 | 5.22E+07 | 6.18E-10 | 6.58E-08 |
| | Day 5 | 5.07E+07 | 7.13E-10 | 5.26E-08 |
| | Day 10 | 4.55E+07 | 3.53E-09 | 3.39E-08 |
| | Day 15 | 4.76E+07 | 1.67E-09 | 3.35E-08 |

## 4.2 Scanning Electron Microscope (SEM)

The epoxy coatings were studied in terms surface morphology by SEM. SEM images showing the surfaces of modified epoxy coatings and neat epoxy coating. The epoxy coating observed to have a relatively smooth surface morphology before immersed in NaCl and no cracks or discontinuities were found as shown in Figure 4.7.

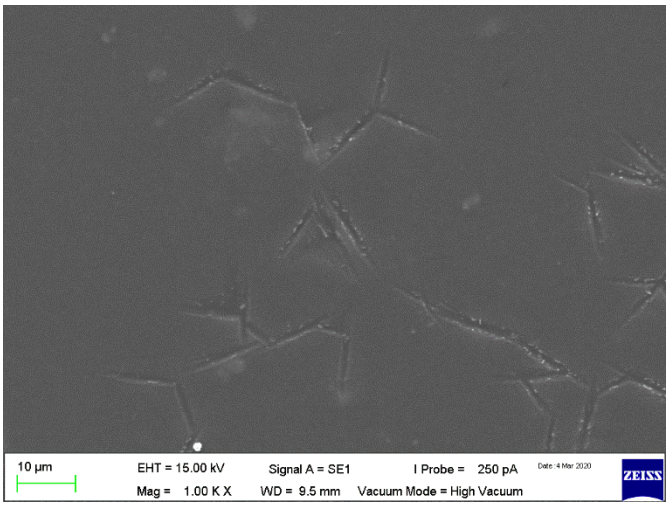



Figure 4. 7: SEM image of epoxy coating with 10wt% ZnO-loaded HNT coating before immersed in NaCl

Moreover, Figure 4.8(a) showed the SEM images of epoxy coatings with different concentration of ZnO-loaded HNT after immersed for 15 days in 3.0wt% NaCl. The surface of EP after immersion observed to have void formation. In addition, cracks also are visible on the surface of EP coating after 15 days of immersion. Thus, formed cracks allow the penetration of water, oxygen and ionic molecule through the coating into the metal surface. When the electrolyte penetrated into the coating system and reached the metal surface, the OH- can be created under the coating. The OH- was created due to the oxygen reduction reaction that occurred at the cathodic sites on the metal surface. Thus, the water molecules might break down the hydrogen bonds between the metal surface and the coating [48].

Besides that, for modified coating exposed in NaCl for 15 days resulted in entirely different morphology with the coating before immersion. SEM images of CEP 1 as presented in Figure 4.8(b) shows the deposition of degraded products on the coating surface. The presence of voids or cracks are not clear in these composite coatings. Next, the surface of CEP10 as shown in Figure 4.8(c) exhibits a layer with

uniform, adherent, and continuous structure and only a little damaged surface occurred compared to neat epoxy and CEP 1. Better surface morphologies of modified coatings compare to neat epoxy might be affected from the existence of nanofillers in the coating system that caused more pathways for the corrosive elements to penetrate the coating system. The results were in line with the EIS result regarding the coating performance.

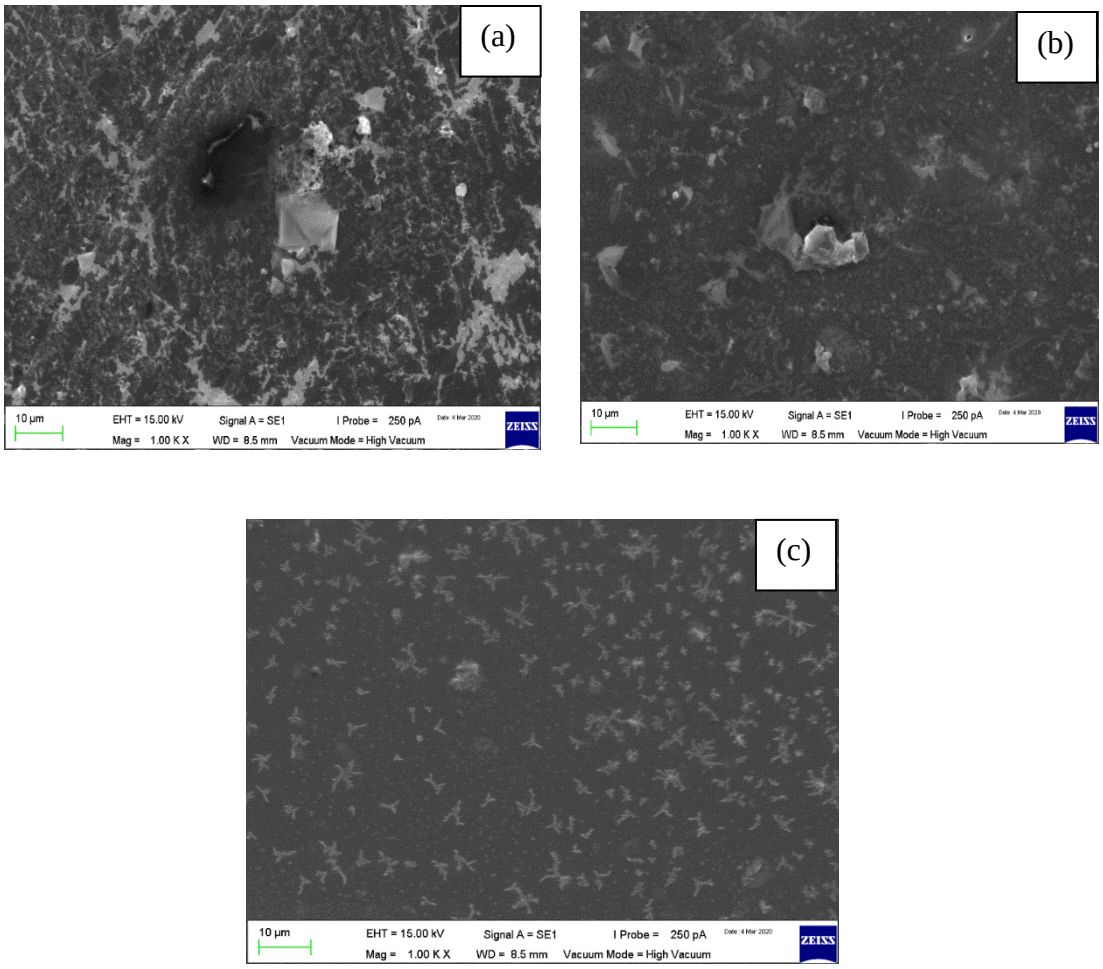



Figure 4. 8: SEM images of epoxy coating surfaces after immersed for 15 days (a)Neat Epoxy (b) 1wt% ZnO-loaded HNT (c) 10wt% ZnO-loaded HNT

# CHAPTER 5

# CONCLUSION AND RECOMMENDATION

## 5.1 Conclusion

The main purpose of this project is to evaluate corrosion protection performance of epoxy coating that contains nanofillers of ZnO and HNT. Investigation on coating performance have been conducted through EIS method to achieve the main objective. From EIS results, all the coatings show a similar trend which the coating resistance decrease along the time of immersion. This might because of the electrolyte penetrate the coating layer and create various depth. However, modified coatings (CEP1, CEP5 and CEP10) showed higher coating resistance for 15 days of immersion in 3.0wt% NaCl as compare to neat epoxy coating (EP). Higher coating resistance proved that modified coatings have better corrosion protection performance than neat epoxy.

In addition, modified coating with 10wt% of ZnO-loaded HNT (CEP10) exhibited the best coating performance. CEP10 showed highest values of coating resistance and reduction in Warburg coefficient which related to enhancement coating resistance due to the role of the nanofillers in the coating. The increment on concentration of ZnO-loaded HNT indicated that the amount of nanofillers affect the coating resistance very much. Thus, modified coating showed better barrier protection properties than neat epoxy.

The surface morphologies of coatings are investigated through SEM. From the results, epoxy coating presented smoother surface before immersed in NaCl. However, the coatings corroded after 15 days of immersion. Neat epoxy coating (EP) showed the worst surface where there are a lot of voids and crack at the surface. In contrast, CEP10 resulted a smooth surface with uniform, adherent, and continuous structure and only a little damaged surface compare to other coatings. As concentration of ZnO-loaded HNT increase, the smoother the surface of the coating after immersion.

Finally, the addition of ZnO and HNT in epoxy coatings showed good performance in enhancing the corrosion protection and improve the barrier properties of the coating in preventing the corrosion at the protected surface.

## 5.2 Recommendations

Some suggestions are encouragingly needed to be included for the future work of this research. The following are some recommendations that could be done to improve this project:

- Coatings with ZnO-loaded HNT should be experiment in various environment such as in high temperature to the expand the application of the modified coatings.
- The exposure time of the coatings should be extending up to 1 month in order to see the trend of the coating resistance.
- Different types of nanocontainers also can be used to evaluate the coatings performance.

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